1039. *Silyl Ethers of Tetrahydro-2-hydroxymethylpyran.*

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Some silyl ether derivatives of tetrahydro-2-hydroxymethylpyran are reported. Toluene-*p*-sulphonylation and vinylation of tetrahydro-2-hydroxymethylpyran, and some derivatives of these compounds, have also been investigated.

RECENT publications[1] have shown the importance of the reaction of silicon-containing compounds with carbohydrates. Hedgley and Overend[1] and Schwarz *et al.*[2] synthesised trimethylsilyl derivatives of some mono- and di-saccharides and recorded their properties. Chang and Hass[3] and Henglein *et al.*[4] independently prepared octa-*O*-(trimethylsilyl)-sucrose. The trimethylsilyl derivatives are generally hydrolysed slowly in moist air and rapidly and quantitatively in boiling aqueous methanol.[1]

The complex nature of the products from sucrose and some alkylchlorosilanes, for example, dimethyldichlorosilane, prompted an investigation of the reaction of some aryl- and alkyl-chlorosilanes with tetrahydro-2-hydroxymethylpyran as model. Other workers[5] have shown that where preferential substitution of the sucrose molecule occurs this involves mainly the primary hydroxyl groupings, although a mixture of products usually results. Thus toluene-*p*-sulphonylation of sucrose with 3 mol. of reagent affords a mixture from which di-, tri-, and tetra-substituted derivatives have been isolated.[5]

Silyl ethers of tetrahydro-2-hydroxymethylpyran (see Table) were prepared essentially by the method described by Henglein *et al.*[4]. In the case of the ether derived from triphenylchlorosilane separation from hexaphenyldisiloxane was necessary. The infrared spectra of the products were in accordance with the proposed structures,[6] showing strong absorptions at 1020—1090 cm.$^{-1}$ (Si–O–C), 1090—1130 cm.$^{-1}$ (Si–Ph), 1250, 841, 754—756 ($SiMe_3$), 1259, 800—814 cm.$^{-1}$ ($SiMe_2$, SiMe).

Tetrahydro-2-tosyloxymethylpyran was prepared according to the method of Eglinton, Jones, and Whiting.[7] Treatment of this compound with sodium iodide in acetone[8] at 100° during 5 hr. afforded tetrahydro-2-iodomethylpyran in high yield. Attempts to cause tetrahydro-2-iodomethylpyran to react with sodium acetylide in liquid ammonia were unsuccessful. This is not wholly due to the low solubility of the iodo-compound in

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[1] Hedgley and Overend, *Chem. and Ind.*, 1960, 378; Sprung, *J. Org. Chem.*, 1958, **23**, 58; Sprung and Nelson, *ibid.*, 1955, **20**, 1770; Burkhard, Schmitz, and Burnett, *J. Amer. Chem. Soc.*, 1953, **75**, 5957; Burkhard, *J. Org. Chem.*, 1957, **22**, 592; Langer, Connell, and Wender, 1958, **23**, 50; Henglein, *Angew. Chem.*, 1958, **70**, 510.

[2] Schwarz, Baronetsky, and Schoeller, *Angew. Chem.*, 1956, **68**, 335.

[3] Chang and Hass, *J. Org. Chem.*, 1958, **23**, 773.

[4] Henglein, Abelsnes, Heneka, Lienhard, Nakhre, and Scheinost, *Makromol. Chem.*, 1957, **24**, 1.

[5] Lemieux and Barrette, *Canad. J. Chem.*, 1960, **38**, 656.

[6] Bellamy, " Infrared Spectra of Complex Molecules," Methuen, p. 334.

[7] Eglington, Jones, and Whiting, *J.*, 1952, 2873.

[8] Tipson, Clapp, and Cretcher, *J. Org. Chem.*, 1947, **12**, 133.

liquid ammonia since no reaction was discernible on addition of ether and dimethylformamide; lithium acetylide [9] similarly did not react.

Mikhant'ev and Lapenko [10] recently prepared vinyl ethers of glucose derivatives by the direct action of acetylene under pressure in the presence of potassium hydroxide at 150—160°. Under similar conditions tetrahydro-2-vinyloxymethylpyran has been obtained in ~44% yield. An alternative route to this vinyl ether involved vinyl-exchange between tetrahydro-2-hydroxymethylpyran and butyl vinyl ether in the presence of mercuric acetate.[11]

An equimolar mixture of the vinyl ether and tetrahydro-2-hydroxymethylpyran in the presence of a trace of hydrochloric acid gave the acetal, 1,1-bis(tetrahydropyran-2-ylmethoxy)ethane. Similar reactions between vinyl ethers and alcohols have been recorded before.[12] Acidic hydrolysis of the acetal yielded acetaldehyde (detected with 4-hydroxybiphenyl) and tetrahydro-2-hydroxymethylpyran.

Reaction of diphenyldichlorosilane with glucose has been shown [4] to yield a polydiphenylsilylglucose. Our results also suggest that certain alkyl- and aryl-chlorosilanes might prove useful cross-linking agents for linear polymers such as cellulose. The mild conditions used in transvinylation might prove useful in the synthesis of vinylated sugar derivatives analogous to those prepared by Mikhant'ev and Lapenko.[10]

EXPERIMENTAL

Silyl ethers were prepared under anhydrous conditions.

Preparation of Silyl Ethers.—The *ethers* (Table), with the exception of that derived from triphenylchlorosilane, were prepared as follows. A solution of dimethyldichlorosilane (12·3 g.) in dry hexane (30 ml.) was added during 20 min. to a stirred solution of tetrahydro-2-hydroxymethylpyran (28 g.) in pyridine (100 ml.). The solution was then cooled and shaken at room temperature for 20 hr. Pyridine hydrochloride was removed and the filtrate concentrated under reduced pressure. The residue was distilled, yielding *dimethylbis(tetrahydropyran-2-ylmethoxy)silane* (21·8 g.), b. p. 134—136°/1·5 mm., n_D^{18} 1·4571 (Found: C, 58·1; H, 9·9. $C_{14}H_{28}O_4Si$ requires C, 58·3; H, 9·7%).

Silyl ethers of tetrahydro-2-hydroxymethylpyran.

No.	Silanes	Yield (%)	B. p./mm.	n_D	Formula
1	Trimethyl(tetrahydropyran-2-ylmethoxy)	71	75—76°/14	1·4320	$C_9H_{20}O_2Si$
2	Dimethylbis(tetrahydropyran-2-ylmethoxy) ...	80	134—136°/1·5	1·4571	$C_{14}H_{28}O_4Si$
3	Methyltris(tetrahydropyran-2-ylmethoxy)	74	170—172°/0·2	1·4683	$C_{19}H_{36}O_6Si$
4	(Tetrahydropyran-2-ylmethoxy)triphenyl	59	(M. p. 52—53°)		$C_{24}H_{26}O_2Si$
5	Bis(tetrahydropyran-2-ylmethoxy)diphenyl ...	85	224—228°/1	1·5380	$C_{24}H_{32}O_4Si$
6	Tris(tetrahydropyran-2-ylmethoxy)phenyl......	79	216—218°/0·05	1·5014	$C_{24}H_{38}O_6Si$
7	Tetrakis(tetrahydropyranylmethoxy)	77	234—236°/1	1·4725	$C_{24}H_{44}O_8Si$

	Found				Required		
No.	C (%)	H (%)	M [a]	Formula	C (%)	H (%)	M
1	57·5	10·75	185	$C_9H_{20}O_2Si$	57·4	10·7	188
2	58·1	9·9	284	$C_{14}H_{28}O_4Si$	58·3	9·7	288
3	58·5	9·1	384	$C_{19}H_{36}O_6Si$	58·8	9·3	389
4	77·2	7·0	369	$C_{24}H_{26}O_2Si$	77·0	6·95	374
5	70·0	7·8	420	$C_{24}H_{32}O_4Si$	70·0	7·8	413
6	64·1	8·3	440	$C_{24}H_{38}O_6Si$	64·0	8·4	451
7	59·2	9·25	498	$C_{24}H_{44}O_8Si$	59·0	9·0	489

[a] Determined by Barger's method.

Tetrahydropyran-2-ylmethoxytriphenylsilane.—A solution of triphenylchlorosilane (32·6 g.,

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[9] Raphael, "Acetylenic Compounds in Organic Synthesis," London, 1955, p. 197.

[10] Mikhant'ev and Lapenko, *Zhur. obshchei Khim.*, 1957, **27**, 2840, 2972.

[11] Watanabe and Conlon, *J. Amer. Chem. Soc.*, 1957, **79**, 2828.

[12] Schostakowsky and Gershtein, *J. Gen. Chem.* (*U.S.S.R.*), 1946, **16**, 937.

0·11 mole) in dry pyridine (100 ml.) was added during 15 min. to a stirred solution of tetrahydro-2-hydroxymethylpyran (12 g., 0·103 mole) in dry pyridine (50 ml.). After refluxing for 4 hr. under anhydrous conditions, the mixture was shaken during 20 hr. The solution was filtered and concentrated under reduced pressure and the solid residue extracted with 7 : 10 v/v toluene–light petroleum (b. p. 40—60°) (85 ml.). The residual solid (2·2 g.) was washed with ether (100 ml.) and methanol (100 ml.) and after drying, had m. p. 223—224°. Its infrared spectrum was identical with that of hexaphenyldisiloxane (lit.,[13] m. p. 221—222°) (Found: C, 80·7; H, 5·7. Calc. for $C_{36}H_{30}OSi_2$: C, 80·9; H, 5·7%). The filtrate and washings were concentrated and on distillation yielded *tetrahydropyran-2-ylmethoxytriphenylsilane* (23 g.), b. p. 234—236°/5 mm., m. p. 52—53° (Found: C, 77·2; H, 7·0. $C_{24}H_{26}O_2Si$ requires C, 77·0; H, 6·95%).

Tetrahydro-2-tosyloxymethylpyran.—This was prepared essentially by the method described [7] and had m. p. 69—70° (lit.,[7] m. p. 72·5°).

Tetrahydro-2-iodomethylpyran.—Tetrahydro-2-tosyloxymethylpyran (4·2 g.) was treated with sodium iodide (8·5 g.) in acetone at 100° during 5 hr. in a sealed tube. The sodium toluene-*p*-sulphonate which separated from the cooled solution was removed and the filtrate diluted with water (*ca.* 150 ml.) and extracted with chloroform (3 × 150 ml.). The combined extracts were washed successively with potassium iodide solution and water and dried (Na_2CO_3). The residue after concentration was shaken with mercury to remove residual iodine and then taken up in a little chloroform and dried (Na_2CO_3). The solvent was removed; the *product* (3·3 g.) had b. p. 60—64°/6 mm., n_D^{24} 1·5341 (Found: C, 31·6; H, 4·8. $C_6H_{11}IO$ requires C, 31·9; H, 4·9%).

Vinylation of Tetrahydro-2-hydroxymethylpyran.—(a) *By acetylene.* A rapid stream of acetylene was passed for 2 hr. through tetrahydro-2-hydroxymethylpyran (27·4 g.) containing potassium hydroxide (3 g.) at 150—160°. The cooled mixture was extracted with ether (5 × 50 ml.), and the extract washed with water (5 × 10 ml.) until the washings were no longer alkaline, and dried ($MgSO_4$). Removal of the solvent under nitrogen gave the vinyl ether admixed with starting material. A portion (8·6 g.) of this residue was chromatographed in light petroleum (b. p. 40—60°) on aluminium oxide (300 g.). Thereafter the desired *product* (2·9 g.) was obtained as a colourless liquid, n_D^{22} 1·4540, with no absorption at *ca.* 3600 cm.$^{-1}$. The percentage unsaturation as determined by iodine titration was 93% (Found: C, 67·9; H, 9·95. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%).

(b) *By transvinylation.* A suspension of mercuric acetate (0·63 g.) in tetrahydro-2-hydroxymethylpyran (5·1 g., 0·044 mole) and butyl vinyl ether (37·2 g., 0·364 mole) was heated under reflux at 125° for 6 hr. Anhydrous potassium carbonate (5 g.) was added to the cooled mixture which was distilled under a reduced pressure of nitrogen directly from the carbonate. The fraction (4·7 g.), b. p. 56—60°/14 mm., was collected and distilled three times from metallic sodium, to yield the product (0·8 g.), b. p. 64°/20 mm., $n_D^{20·5}$ 1·4544. The percentage unsaturation as determined by iodine titration was 97% (Found: C, 67·9; H, 9·95%).

1,1-*Bis*(*tetrahydropyran*-2-*ylmethoxy*)*ethane.*—A crude sample of the above vinyl ether (1 g., 79% unsaturation) was added to tetrahydro-2-hydroxymethylpyran (0·83 g.) with cooling to 0°, and one drop of concentrated hydrochloric acid was added. After 24 hr. the mixture was distilled, to give the *product* (0·54 g.), b. p. 176°/20 mm., n_D^{19} 1·4654 (Found: C, 64·9; H, 10·1. $C_{14}H_{26}O_4$ requires C, 65·1; H, 10·15%).

The dry acetal (0·15 g.) was treated under reflux with 2N-hydrochloric acid for 2 hr. The cooled hydrolysate gave a characteristic violet colour with 4-hydroxybiphenyl in concentrated sulphuric acid, indicating presence of acetaldehyde. The reaction mixture was extracted with ether (3 × 20 ml.) and dried (K_2CO_3). The liquid remaining after removal of the solvent had the infrared spectrum of tetrahydro-2-hydroxymethylpyran.

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[13] Dilthey and Eduardoff, *Ber.*, 1904, **37**, 1139; Schumb and Saffer, *J. Amer. Chem. Soc.*, 1941, **63**, 93.